

[J. Chem. Soc., Perkin Trans. I, 915 (1990)]

Reactivity of 10-Thiaisoalloxazine. Ring-contraction by Water (Hydroxide Ion) followed by Redox Reaction.

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Heating of 3-methyl-10-thiaisoalloxazine (1) in aqueous acetonitrile results in the formation of 1,5-dihydro-3-methyl-10-thiaisoalloxazine (3), 1'-methylspiro(2,3-dihydrobenzothiazole-2,5'-pyrimidine)-2', 4', 6'-trione (4), and 1-(benzothiazol-2-yl) carbonyl-3-methylurea (5). In sharp contrast, 3,10-dimethylisoalloxazine (2) is very stable under the conditions employed. Experimental results document that the formation of (3) and (5) arises from a redox reaction between the ring-contracted product (4), initially produced by hydrolysis of (1), and unreacted (1). These reaction can be attributed to the increased susceptibility of (1) to nucleophilic addition and its higher oxidation capacity compared to the isalloxazine (2).

[J. Chem. Soc., Perkin Trans. I, 3339 (1990)]

Photochemical Oxygenation of Phenols by Pyrimido [5,4-*g*]pteridine *N*-Oxide. Comparative Studies with Pyridazine and Isoalloxazine *N*-Oxides.

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1,3,7,9-Tetrabutylpyrimido [5,4-*g*] pteridine-2,4,6,8(1*H*, 3*H*, 7*H*, 9*H*)-tetrone 5-oxide (1) transfers its *N*-oxide oxygen to phenols, *i.e.*, phenol, *p*-cresol, *L*-tyrosine methyl ester, and *p*-hydroxyacetanilide (acetaminophen), under photochemical conditions to give the corresponding dihydric phenols as major products. The oxygenation is reasonably explained in terms of a photo-induced single-electron transfer (SET) followed by oxygen-atom transfer (the SET mechanism) which occurs *via* the initial formation of a charge-transfer complex between (1) and the phenols employed. Comparative experiments with 3,10-dibutylisoalloxazine 5-oxide and 3-methylpyridazine 2-oxide well demonstrate the simplicity and the mechanistic characteristics of the photochemistry of (1).

[Chem. Pharm. Bull., 38, 2069 (1990)]

Photo-oxygenation of Alkanes by a Heterocyclic *N*-Oxide *via* Non-oxene Mechanism. Peculiar Photochemical Property of Pyrimido [5,4-*g*] pteridine *N*-Oxide.

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Irradiation of a solution of cyclohexane (2) or adamantane (3) in chloroform containing pyrimido [5,4-*g*] pteridine *N*-oxide (1) with UV-visible light resulted in the formation of the corresponding oxygenated products [cyclohexanol and cyclohexanone from (2); 1- and 2-hydroxyadamantanes and 2-oxoadamantane from (3)] together with chlorinated products [chlorocyclohexane and hexachloroethane (4) from (2); 1- and 2-chloroadamantanes and (4) from (3)]. The present observation further demonstrates the peculiar photochemical property of (1) in comparison with the heterocyclic *N*-oxides so far investigated and indicates that an excited (1) functions as a radical initiator and an oxygen-atom donor to the non-activated alkanes in chloroform.